

The Electrolytic Properties of Dilute Solutions of Sulphuric Acid

W. C. D. Whetham and H. H. Paine

Proc. R. Soc. Lond. A 1908 **81**, 58-80

doi: 10.1098/rspa.1908.0063

Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

To subscribe to *Proc. R. Soc. Lond. A* go to: <http://rspa.royalsocietypublishing.org/subscriptions>

The Electrolytic Properties of Dilute Solutions of Sulphuric Acid.

By W. C. D. WHETHAM, M.A., F.R.S., and H. H. PAINE, B.A.,
Trinity College, Cambridge.

(Received June 4,—Read June 18, 1908.)

Part 1.—By W. C. D. WHETHAM.

1. *The Electrical Conductivities.*

The first section of the present paper contains an account of a continuation of the work described in the 'Proceedings of the Royal Society,' A, vol. 76, p. 577, 1905, and a statement of the object of the investigation may be reproduced from that place:

"If the measure of the electrical conductivity of a solution be divided by that of the concentration expressed in gramme-equivalents per unit volume, we obtain a quantity which may be called the equivalent conductivity of the solution. If the conductivity of the solvent used be subtracted from that of the solution, the corresponding quantity may be taken as giving the equivalent conductivity of the solute.

"As is well known, the equivalent conductivity of neutral salts when dissolved in water approaches a limiting value as the dilution is increased, and, in terms of the ionisation theory, this limiting value corresponds with complete ionisation.

"With solutions of acids and alkalies, however, the phenomena are different. As dilution proceeds, the equivalent conductivity reaches a maximum at a concentration of about a one-thousandth or a two-thousandth of a gramme-equivalent per litre, and then falls rapidly as the dilution is pushed farther.

"It has been supposed that this diminution of equivalent conductivity at extreme dilutions is due to interaction between the solute and the impurities which remain even in redistilled water.

"Kohlrausch has given evidence to show that the chief impurity in water carefully redistilled is carbonic acid," but the experiments described in the writer's former paper show that no appreciable change in the phenomenon is produced by boiling the water used as solvent repeatedly under low pressure, and re-admitting the air through potash bulbs. This process would remove a great part at least of the carbonic acid in the solvent, and it causes a large diminution in the conductivity of the water, but, on adding small

Electrolytic Properties of Dilute Solutions of Sulphuric Acid. 59

quantities of sulphuric acid to solvent so purified, a conductivity curve of the normal type is obtained—the lowering of equivalent conductivity at great dilution is not affected appreciably. The first step in continuing the research consisted in repeating the process of boiling the solvent under diminished pressure, but in re-admitting air through bulbs containing dilute sulphuric acid as well as others containing potash. Any volatile alkaline impurity such as ammonia would thus partly be removed, and, if such impurity were the cause of the phenomenon, the conductivity curves obtained by adding acid to the purified solvent would be modified.

The following results were obtained—

Number of solution.	Concentration (gramme-equivalents per 1000 grammes of solution = m).	$m^{\frac{1}{3}}$.	Conductivity at 18° C. in arbitrary units = k .	Conductivity less that of solvent = k_0 .	Equivalent conductivity of sulphuric acid = k_0/m .
0	0.0	—	1.041×10^{-5}	—	—
1	4.812×10^{-5}	0.03638	1.800×10^{-4}	1.696×10^{-4}	3.526
2	9.158×10^{-5}	0.04506	3.542×10^{-4}	3.438×10^{-4}	3.757
3	1.983×10^{-4}	0.05831	7.817×10^{-4}	7.713×10^{-4}	3.890
4	3.579×10^{-4}	0.0710	1.413×10^{-3}	1.403×10^{-3}	3.936
5	6.523×10^{-4}	0.0935	2.543×10^{-3}	2.533×10^{-3}	3.910

As comparative numbers only were needed, the conductivities were expressed in arbitrary units—the reciprocals of the measured resistances in the cell employed. It will be seen that the usual phenomenon of a fall in the equivalent conductivity at great dilution is still evident, and the curve obtained by plotting $m^{\frac{1}{3}}$ and k_0/m is not appreciably different from that obtained when unboiled distilled water is used as solvent.

Thus the efforts made to remove residual ammonia are without result on the conductivity of solutions of sulphuric acid made up with the solvent so purified.

Hence it seems that traces in the solvent neither of carbonic acid nor ammonia are competent to explain the peculiarities in the conductivity of dilute solutions of acids. As will be pointed out in Part 2 of this paper, however, another possibility remains, namely, the presence in redistilled water of traces of carbonate or bicarbonate of ammonia. Such an impurity might produce the effect observed both with acids and with alkalies, and the slight trace of it requisite might not be removed by treatment such as is described above. However this may be, it seems unlikely that the impurity which is usually assumed to be the cause of the phenomenon is competent to explain it.

2. *The Transport Ratios.*

If the phenomenon of the decrease in equivalent conductivity be not due to impurities in the solvent, it must be caused by some change in the conductivity of the solute itself. A decrease in conductivity must be accompanied by a decrease in the effective velocity of one or both of the ions. Since the phenomenon under investigation occurs with alkalies as well as acids, it seems likely that, if it be not due to impurities, it depends on the presence of the one ion in each of these classes of compounds which is identical with one of the ions of the solvent—in acids the hydrogen ion, and in alkalies the hydroxyl ion. Hence, on the supposition we are now making, it is probable that one ion would be affected in a different way to the other. We may expect that in solutions of acids the hydrogen ion travels slower at great dilutions than at more moderate concentrations. Such a differential treatment of the ions would be made manifest by a determination of the migration constant or transport ratio of solutions of different concentrations. If an electric current be passed through a solution between non-dissolvable electrodes, solute is lost from the solution in the neighbourhood of both electrodes, and it is readily shown that the ratio of loss is equal to the ratio between the opposite ionic velocities. The ratio of the velocity of the anion to the sum of the velocities is taken as the transport ratio or migration constant. A decrease in the velocity of the hydrogen ion of acids, then, would cause an increase in the measured transport ratio.

The transport ratio usually has been measured by determining the concentration of the solution by chemical means before and after the passage of the current in the neighbourhood of the two electrodes. But, in the present case, the concentrations involved were far too small to be estimated chemically; it was necessary to devise a new method.

Now, in the measurement of electrical conductivity, we possess a means of determining the concentration of a dilute solution much more sensitive and accurate than any method of chemical analysis, and a method of experimenting was designed to utilise these advantages.

Fig. 1 shows a cell made of Jena glass. It consists of two vertical tubes connected horizontally through an inverted **V**, to the apex of which a quill tube of glass is fused. To this quill tube is fixed a piece of rubber tubing, and by a slight increase of air pressure the level of the liquid in the inverted **V** can be depressed so as to separate the liquid into two parts, one confined to each vertical limb of the apparatus.

In each vertical tube are placed two platinum electrodes, carried by glass tubes through the ends of which stout platinum wires are sealed. By

measuring the resistance between these electrodes, the specific resistance of the solution round them can be determined, while, if each pair of electrodes is connected electrically together, a current may be passed through the whole apparatus from one pair of electrodes to the other when the liquid fills the inverted V-tube as well as the vertical limbs.

The electrodes in the side tubes lie just above the junctions with the connecting tube. By this arrangement the danger of convection currents, leading to a mixture of the anode and cathode portions of the solution, is avoided, for, in the cathode region, where the concentration diminishes, the lighter liquid rises towards the surface, while the denser anode liquid has no tendency to pass into the rising connecting tube, and sinks to the bottom of the side limb of the apparatus. The influence of diffusion was shown to be negligible in the course of the experiments, for identical results were obtained in similar experiments of long and short duration, in which the effects of diffusion would differ.

The mode of procedure is as follows: A solution of pure potassium chloride is made up of a convenient strength by weighing out the salt. This solution is diluted by adding a known weight of water. The resistance of the solution so prepared, when placed in the cell, is measured between each pair of electrodes. From the specific resistance of potassium chloride solutions, as given by Kohlrausch, this gives the cell constant of each end of the apparatus, treating each vertical limb as a separate resistance cell. After careful washing, the apparatus is then filled with a solution of sulphuric acid, the concentration of which is known to be approximately that required. By measuring the resistance between each pair of electrodes, two values for the exact concentration may then be calculated from Kohlrausch's tables.

The apparatus is now ready for a migration experiment. A current from

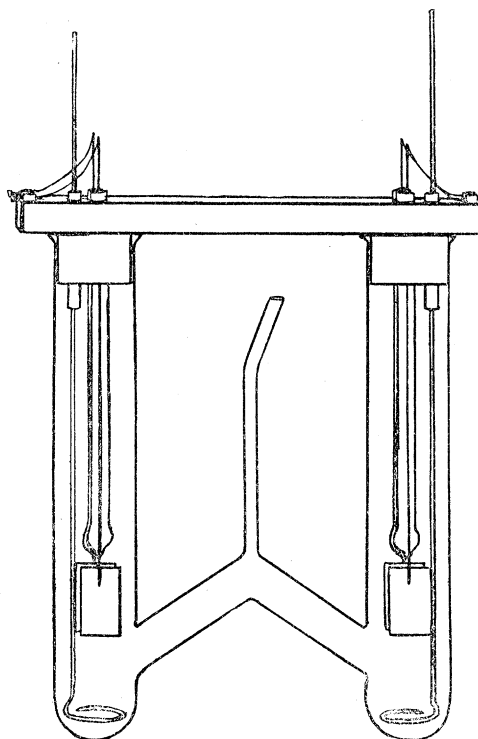


FIG. 1.

a battery of 50 or 100 small storage cells is passed through the apparatus from one pair of electrodes to the other, each pair, in this part of the work, being used as a single electrode. The strength of the current is determined by passing it through a standardised shunted galvanometer, and thus the total amount of chemical decomposition calculated from the known values of the electro-chemical equivalents. After a definite time has elapsed, the circuit is broken, the two parts of the solution are separated by increasing the pressure of the air in the inverted V-tube, and measurements are taken of the resistance between each pair of electrodes as before. The change in concentration in the solution round each electrode may thus be estimated, and, by extracting and weighing each part of the solution, the total change in contents of acid calculated.

In a solution of sulphuric acid, the ions are hydrogen and the sulphion group SO_4 . Hydrogen is liberated as such at the cathode, but the sulphion reacts with the water to form sulphuric acid and oxygen, the latter escaping. Thus when one gramme-equivalent of hydrogen is evolved, one gramme-equivalent of acid is reformed at the anode by the secondary action of the sulphion and the water. But, besides this change, that due to migration must be considered. If the cation of any salt solution drifts one way with a velocity u , and the anion the other with a velocity v , the amount of separation in unit time is $u+v$. In accordance with the principle of migration, there is a loss of salt measured by v at the cathode, and a loss measured by u at the anode. But in our case there is also a gain of $u+v$, equal to the total amount of decomposition, at the anode. Thus the resultant gain at the anode is $u+v-u$ or v , and the resultant loss at the cathode is also v . Hence, by determining the loss and gain, we get two independent values for the same quantity, and the concordance between them gives a preliminary test of the success of the apparatus and method.

Finally, a knowledge of the value of the current and its time of flow gives $u+v$, and enables us to calculate $v/(u+v)$, the transport ratio.

After some changes, the apparatus in its final form gave satisfactory results as tested by the agreement between the loss of acid at the cathode and the gain at the anode. Details of one experiment may be given as an example.

Resistances before passage of current	{	Anode vessel ... 7102, 7106, 7112 = 7107
		mean in ohms
	{	Cathode „ ... 6252, 6258, 6264 = 6258
		mean in ohms.

1908.] *Properties of Dilute Solutions of Sulphuric Acid.*

63

Current from 50 cells (= 100 volts) passed for 15 minutes—

Resistances... $\begin{cases} \text{Anode vessel, } 8316, 8263, 8296 = 8297 \\ \text{Cathode „ } 5452, 5461, 5464 = 5462 \end{cases}$

Weight of solutions in anode vessel = 53.25 grammes.

Weight of solutions in cathode „ = 57.00 „

From these results it follows that the conductivity of the solution before the passage of the current was 1.408×10^{-5} .

After the passage of the current the conductivity of the anode solution was 1.614×10^{-5} , and of the cathode solution 1.219×10^{-5} .

The concentration of the original solution was 4.042×10^{-5} gramme-equivalent per 1000 grammes. From the known curve between concentration and equivalent conductivity, the concentration of the final anode and cathode solutions was estimated as 4.575×10^{-5} and 3.546×10^{-5} respectively. Then, from the observed total masses of their solutions, the total gain and loss in contents was calculated as 2.843×10^{-7} gramme-equivalent and 2.831×10^{-7} gramme-equivalent respectively.

A rough estimate of the current gave 1.491×10^{-4} ampere, and, as the total number of gramme-equivalents liberated, 1.390×10^{-6} . Thus the transport ratio is approximately $0.2836/1.390 = 0.205$.

No stress can be laid on this last result, as the method of measuring the current was not that finally adopted as satisfactory, but the concordance between the gain of acid at the anode and the loss at the cathode showed that, so far, the method was successful.

At this point the pressure of other duties prevented the writer from continuing the experiments, but, by the aid of the Government Grant Committee of the Royal Society, the services of Mr. H. H. Paine were secured. The work described in Part 2 of this paper is Mr. Paine's; the present writer only exercised a general supervision over the course of the research.

Part 2.—By H. H. PAINE.

1. *Method of Experiment.*

The migration constant was determined for solutions of sulphuric acid of concentration varying from 0.1 to 0.00005 normal. A current, the strength of which was determined by means of a standardised galvanometer, was passed through the migration cell, and the total change in the quantity of solute round the anode and cathode measured. As explained in the first part of this paper, the value of this change in gramme-equivalents, divided by the number of gramme-equivalents of hydrogen evolved at the cathode, gives us the migration constant for the solution.

The great advantage of sulphuric acid for these experiments is that no uncertain reactions take place at either anode or cathode. Measurements of the change in concentration at the two electrodes are thus equally trustworthy, and each serves as a check on the other.

The solutions used were made up with water having a specific conductivity of from 0.9×10^{-6} to 1.0×10^{-6} reciprocal ohm at 18°C . Ordinary distilled water was redistilled in a Jena glass apparatus with a trace of sulphuric acid and of potassium bichromate. A stock solution of sulphuric acid (of strength about 0.1 normal) was prepared from some pure 50 per cent. sulphuric acid supplied by Messrs. Baird and Tatlock. The conductivity of this solution was measured, and its exact strength thence determined by means of Kohlrausch's tables. Dilute solutions were obtained from this by taking a weighed quantity and adding the requisite amount of water.

After the passage of the current through the migration cell, the strengths of the solutions in the anode and cathode regions were determined by measuring their conductivities. For this purpose it is necessary to know how the conductivity varies with concentration. The relation between the two has been determined by several observers, and the results plotted in the form of a curve showing the ratio of the equivalent conductivity to the cube root of the concentration. It was thought advisable, however, to have such a curve for the actual solution under observation. Since the solutions were all made up gravimetrically from the original one, we have at once a means of finding the concentration (in terms of that of the original). The conductivity was also measured. Each solution made up thus gave a point on the curve. From the curve so drawn, calculations were made for determining the strengths of the two solutions after the passage of the current. Slight effects due to the solution of impurities during the course of the experiment would give too small a value for the change in concentration on the one side, and too large a value on the other; taking the mean, therefore, tends to eliminate these effects; agreement between the changes on the two sides is a sure test that such errors have not entered to vitiate the results. This is a very important consideration, for with such weak solutions as were used, fouling, not only by the solution of solid matter from the surface of the vessel, but also by the absorption of gases such as ammonia from the air, is very likely to occur. Without such a check it would be dangerous to draw any conclusions as to the value of the migration constant for solutions weaker than 0.0001 normal, whereas with the help of this check successful experiments were conducted with solutions as weak as 0.00005 normal.

2. *Apparatus.*

1. *Conductivity Cells.*—Two cells were used in the course of the experiments for the purpose of measuring the conductivity, one for the two strongest solutions (0.1 and 0.01 N.) and the other for solutions of strength 0.001 N. and under.

The electrodes in both cells were of platinum, but in the case of the cell used for the stronger solutions (fig. 2), they were coated with platinum-black, while in the other cell (fig. 3), after platinisation, they had been heated to redness before being sealed into the glass. In the second cell, contact with the electrodes was made by means of mercury poured into the side

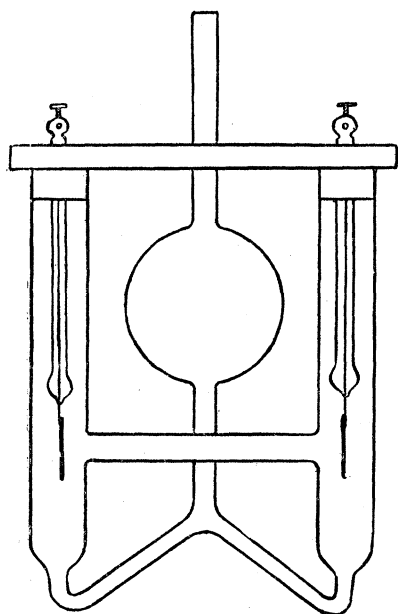


FIG. 2.

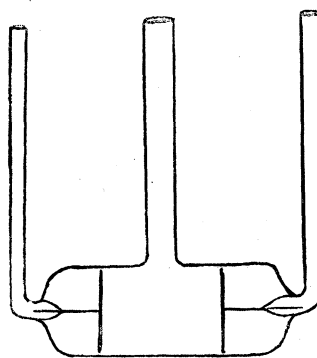


FIG. 3.

tubes. The centre tube leading to the cell-chamber was closed with a glass cap, by the use of which, it was found, fouling from the atmosphere was prevented completely.

The cell-constant for each cell was determined by means of a standard potassium chloride solution made up from the carefully prepared, pure, crystallised salt. Knowing the concentration of this solution, we can calculate its conductivity (in reciprocal ohms) from the tables compiled by Kohlrausch.

The resistance in each case was determined by the method of Wheatstone's bridge. By the use of the commutator described in a paper by one of the

authors,* an alternating current was obtained, and at the same time a galvanometer used for testing the balance. The commutator was driven at the requisite speed by means of a small electric motor. In all measurements of the resistance the cell was placed in a bath of water kept well stirred and maintained at a temperature of 18°C ., as shown by a Beckmann thermometer reading to hundredths of a degree. The temperature of the solution was regarded as constant and uniform when the measured resistance remained unaltered with time.

2. *The Migration Cell*.—This has been described in the first part of the paper. It may further be noticed here that by placing a pair of electrodes on each side, it was possible to measure the resistances of both portions of the liquid immediately before and immediately after the passage of the current, without transference to other conductivity cells. An almost certain cause of fouling was thus avoided. This device could be employed only for the weaker solutions (0.0002 N. and under), as the resistances in the case of stronger solutions would be too small to be measured accurately with these electrodes. But with the stronger solutions any possible fouling on transfer would be inappreciable.

3. *Galvanometer*.—The current through the migration cell was measured by means of a Nalder's moving-coil galvanometer, which, with the shunts used in the experiment, was previously standardised. This was done in the following way:—A current from a single storage cell (with a suitable resistance in series) was passed through a milliampere- (or volt-) metre, of resistance exactly 1 ohm. The terminals of the galvanometer were connected with the terminals of the ampere-metre through convenient resistances. From the reading of the ampere-metre and a knowledge of the resistance in the galvanometer circuit, we can calculate the current through the galvanometer. The deflections of the suspended coil of the galvanometer (observed by the ordinary reflection method) were noted simultaneously.

3. *Experimental Details.*

The method of procedure for solutions of strengths 0.0005 normal and over differed slightly from that for weaker solutions. In the case of the stronger solutions the conductivity was too great for the resistance to be measured by means of the electrodes in the migration cell. Hence the liquid had to be transferred to a conductivity cell. The conductivity of the original solution was first determined in one of these cells, in order to obtain a point on the equivalent conductivity curve. Some of the solution was then poured into the migration cell until the connecting tube was completely

* 'Phil. Trans.,' A, 1900, vol. 259, p. 321.

1908.] *Properties of Dilute Solutions of Sulphuric Acid.* 67

filled. The current (supplied by a hundred small storage cells) was passed through the apparatus for a time (generally 10 to 15 minutes) sufficient to produce on the average a 10 per cent. change in the strength of the solutions, that is to say, until 10 per cent. of the sulphate ions on the cathode side had migrated to the anode region. When the current had been stopped, the air pressure in the inverted V-tube was raised until the liquid had been forced to the ends of the tube, thus separating the anode and cathode portions. Each portion was then well stirred, and afterwards transferred by means of a syphon to a weighed flask, the syphon and flask having been carefully rinsed with pure water, and dried, before using. After the weight had been taken, the solution was poured into the conductivity cell, and its resistance measured.

For solutions weaker than 0.0005 normal, the initial conductivity was determined in the conductivity cell as before. After the solution had been poured into the migration cell, the air pressure in the inverted V-tube was raised until the liquid had descended to the ends of the tube. The resistance on each side was measured, the solution being well stirred, and the temperature maintained at 18° C. After the air pressure had been released, and the liquid had risen to its former level, the current was passed through for the required time. The anode and cathode portions were again separated, as at the beginning of the experiment, and the resistances measured. Finally, the two portions were separately drawn off by means of a syphon, and weighed. The final conductivities are easily calculated, from the fact that they bear to the initial conductivity the ratios of the resistances (measured in the migration cell) at the beginning to those at the end of the experiment.

In calculating the conductivity of the sulphuric acid, the conductivity of the solvent was deducted from that of the solution in every case.

4. *Experimental Results.*

The following example shows the complete method of calculation for one of the experiments:—

Solution 20.

Original strength (as made up from a standard solution).....	1.0140×10^{-7} grm.-equiv. per c.c. ($= m_0$)
Resistance in conductivity cell	12,916 ohms
Cell-constant.....	0.4532
Conductivity of solution.....	$\frac{0.4532}{12916}$
	$= 3.509 \times 10^{-5}$ recip. ohm
Conductivity of water (solvent).....	0.103
Conductivity of acid (solute)	3.406×10^{-5} „ ($= k_0$)
(Hence $k_0/m_0 = 336.0$,	$\sqrt[3]{m_0} = 0.0466$.)

	Anode region.	Cathode region.
Resistances in migration cell, before ...	4825 ohms	5012 ohms
after	4276 „	5716 „
Weights of solutions	53.74 grammes	55.56 grammes
<i>Calculations.—Anode side.—</i>		
Conductivity after experiment	$3.509 \times 10^{-5} \times \frac{4825}{4276}$	
	$= 3.959 \times 10^{-5}$ recip. ohm	
Conductivity of water	0.103	
Conductivity of acid (solute)	$3.856 \times 10^{-5} (= k_a)$	
Concentration from curve $\left(\frac{k_a}{(k/m)}\right)$	$\frac{3.856 \times 10^{-5}}{339.0}$	
	$= 1.1377 \times 10^{-7}$ gm.-equiv. per c.c.	
Increase in concentration	0.1237×10^{-7}	
Total increase in quantity of acid	$0.1237 \times 10^{-7} \times 53.74$	
	$= 0.665 \times 10^{-6}$ gm.-equiv.	
<i>Cathode side.—</i>		
Conductivity after experiment	$3.509 \times 10^{-5} \times \frac{5012}{5716}$	
	$= 3.077 \times 10^{-5}$ recip. ohm.	
Conductivity of water	0.103	
Conductivity of acid (solute)	2.974×10^{-5} „ $(= k_c)$	
Concentration from curve $= \left(\frac{k_c}{(k/m)}\right)$...	$\frac{2.974 \times 10^{-5}}{332.0}$	
	$= 0.8960 \times 10^{-7}$ gm.-equiv. per c.c.	
Decrease in concentration	0.1180×10^{-7}	
Total increase in quantity of acid	$0.1180 \times 10^{-7} \times 55.56$	
	$= 0.655 \times 10^{-6}$ gm.-equiv.	
Mean of change for two sides	0.660×10^{-6} gm.-equiv.	
Current through cell	4.53×10^{-4} ampere	
Flowed for 12 mins.	$= 720$ secs.	
Hence number of gm.-equiv. of hydrogen liberated		
	$= 4.53 \times 10^{-4} \times 720 \times 1.036 \times 10^{-5} = 3.38 \times 10^{-6}$	
Migration constant or transport ratio	$= \frac{0.660 \times 10^{-6}}{3.38 \times 10^{-6}} = 0.195.$	

The following table contains the results of the whole series of experiments ; its various columns will easily be understood from the preceding example. In deducing the mean of the several values for the migration constant at any particular concentration, those experiments were regarded as most trustworthy for which the calculated changes at anode and cathode were most nearly equal, and the values for the migration constant were weighted accordingly. The difference between the weighted mean and the actual one was always quite small.

The solution 0.0001 normal was the strongest for which the conductivity could be measured in the migration cell itself. Hence, for the solution 0.0002 normal, in the case of which the anode and cathode portions had to

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Number of solution.	Initial concentration (gramme-equivalent per litre).	Total change in quantity of H_2SO_4 (gramme-equivalent).			Gramme-equivalent of hydrogen liberated at cathode.	Migration constant (from Columns V and VI).	Weighted mean.
		Anode.	Cathode.	Mean.			
1	1.0465×10^{-1}	4.47×10^{-4}	4.67×10^{-4}	4.57×10^{-4}	2.485×10^{-3}	0.184	0.186
2	1.0465×10^{-1}	5.71×10^{-4}	5.83×10^{-4}	5.77×10^{-4}	3.079×10^{-3}	0.187	
3	1.0070×10^{-2}	5.82×10^{-5}	6.14×10^{-5}	5.98×10^{-5}	3.214×10^{-4}	0.186	0.186
4	1.0070×10^{-2}	8.65×10^{-5}	8.96×10^{-5}	8.80×10^{-5}	4.744×10^{-4}	0.1855	
5	1.0230×10^{-3}	5.50×10^{-6}	5.71×10^{-6}	5.60×10^{-6}	2.71×10^{-5}	0.206	0.189
6	1.0230×10^{-3}	5.49×10^{-6}	5.64×10^{-6}	5.56×10^{-6}	2.96×10^{-5}	0.188	
7	1.0255×10^{-3}	5.49×10^{-6}	5.51×10^{-6}	5.50×10^{-6}	2.93×10^{-5}	0.188	0.185
8	1.0255×10^{-3}	4.09×10^{-6}	4.13×10^{-6}	4.11×10^{-6}	2.13×10^{-5}	0.193	
9	1.0165×10^{-3}	3.37×10^{-6}	3.49×10^{-6}	3.43×10^{-6}	1.864×10^{-5}	0.184	0.1855
10	1.0165×10^{-3}	3.52×10^{-6}	3.48×10^{-6}	3.50×10^{-6}	1.864×10^{-5}	0.188	
11	1.0165×10^{-3}	3.90×10^{-6}	3.92×10^{-6}	3.91×10^{-6}	2.11×10^{-5}	0.185	0.194
12	0.5133×10^{-3}	2.57×10^{-6}	2.59×10^{-6}	2.58×10^{-6}	1.402×10^{-5}	0.184	
13	0.5133×10^{-3}	3.77×10^{-6}	3.83×10^{-6}	3.80×10^{-6}	2.05×10^{-5}	0.185	0.202
14	0.5081×10^{-3}	2.89×10^{-6}	3.02×10^{-6}	2.955×10^{-6}	1.582×10^{-5}	0.187	
15	0.20785×10^{-3}	0.644×10^{-6}	0.596×10^{-6}	0.620×10^{-6}	3.40×10^{-6}	0.182	0.207
16	0.20785×10^{-3}	1.008×10^{-6}	0.963×10^{-6}	0.985×10^{-6}	5.25×10^{-6}	0.188	
17	0.20785×10^{-3}	1.100×10^{-6}	1.022×10^{-6}	1.061×10^{-6}	5.70×10^{-6}	0.184	0.203
18	1.0140×10^{-4}	5.765×10^{-7}	5.625×10^{-7}	5.695×10^{-7}	2.93×10^{-6}	0.195	
19	1.0140×10^{-4}	5.15×10^{-7}	5.18×10^{-7}	5.165×10^{-7}	2.69×10^{-6}	0.192	0.200
20	1.0140×10^{-4}	6.65×10^{-7}	6.55×10^{-7}	6.60×10^{-7}	3.38×10^{-6}	0.195	
21	0.5440×10^{-4}	3.18×10^{-7}	3.25×10^{-7}	3.215×10^{-7}	1.566×10^{-6}	0.205	0.191
22	0.5440×10^{-4}	3.78×10^{-7}	3.78×10^{-7}	3.78×10^{-7}	1.827×10^{-6}	0.207	
23	0.5405×10^{-4}	2.83×10^{-7}	2.83×10^{-7}	2.83×10^{-7}	1.392×10^{-6}	0.203	0.201
24	0.5405×10^{-4}	3.01×10^{-7}	3.08×10^{-7}	3.045×10^{-7}	1.522×10^{-6}	0.200	
25	0.5832×10^{-4}	2.62×10^{-7}	2.56×10^{-7}	2.59×10^{-7}	1.359×10^{-6}	0.191	0.202
26	0.5832×10^{-4}	5.58×10^{-7}	5.50×10^{-7}	5.54×10^{-7}	2.756×10^{-6}	0.201	

be transferred to the conductivity cell, and for which the discrepancies between the changes on the two sides were rather large, the value obtained for the migration constant is not very trustworthy. Of the three experiments performed with this solution, that showing the best agreement between the

measured changes at the anode and cathode is the one giving 0.188 as the migration constant.

It was found that the conductivities of solutions of the same strength made up with different specimens of distilled water were not the same. When the discrepancy was small, the procedure adopted in calculation was as follows. From the conductivity of the solution a value for the concentration was calculated from the curve which had been already drawn. Let m be this value, and m_0 the true concentration. Then, from the standpoint of the conductivity curve, m_0 gramme-equivalents behave as though they were m gramme-equivalents. Hence, concentrations deduced from the curve were multiplied by the factor m_0/m to get the true concentrations. We get practically the same result, if, calculating k/m_0 for the solution, we increase or decrease the ordinates of the curve (by some fixed length) until it passes through the point showing the true value of k/m for the solution, and calculate concentrations from this curve. The corrections made in this way were only small ones, so that, though the method of correcting has no very firm theoretical basis, it is probably accurate enough for the purpose.

In the case of one or two of the weakest solutions made up six or seven weeks after the rest of the experiments had been performed, the discrepancy was rather large. For these solutions fresh conductivity curves were plotted (from direct experiment) which passed very near the points corresponding to the new solutions, and from these curves the "final concentrations" were calculated for these solutions.

It will be noticed that some of the values for the transport ratio are abnormally divergent from the mean. There was nothing in the course of these particular experiments to lead one to regard the results as untrustworthy. An explanation of the divergence will be suggested later. In deducing the "mean" of the results of individual experiments, however, no account was taken of this explanation; the final results, therefore, are purely experimental.

5. *Theoretical Considerations.*

These experiments seem to show an increase in the migration constant at extreme dilutions. If this be due to the falling-off in velocity of the hydrogen ion, we can calculate what the rise in the migration constant should be in order to account for the drop in the equivalent conductivity curve. To do this, it is necessary to make some assumption as to the cause of the smaller velocity of the hydrogen ion, and so deduce what the conductivity would have been if the velocity had remained unaltered. It has long been noticed that the phenomenon under investigation is observed

1908.] *Properties of Dilute Solutions of Sulphuric Acid.* 71

only for acids and alkalies, *i.e.*, those substances which in solution form hydrogen or hydroxyl ions, the ions of the solvent. Considerations of mass action show at once that the ionisation of the water is greatly reduced by the presence of a trace of acid or alkali. The greater the concentration of the acid, the smaller will be the ionisation of the water. Assuming that the conductivity of Kohlrausch's purest water (0.87×10^{-7}) gives us approximately a measure of its ionisation in these conditions, it may be shown that for concentrations of acid or alkali greater than 10^{-7} gramme-equivalent per litre, the number of hydroxyl or hydrogen ions from the water is inversely proportional to the quantity of acid or alkali in solution.

If the diminution in the equivalent conductivity of acid solutions at extreme dilutions be caused by the water itself rather than by impurities, it is reasonable to suppose that the effect would be directly proportional to the ionisation of the water, and hence inversely proportional to the concentration of the acid, the effect becoming greater as the dilution proceeds. Now, if at points along the equivalent conductivity (k/m) curve we add ordinates proportional to the concentration of the hydroxyl ions (*i.e.*, inversely proportional to the concentration of the acid), we obtain another curve. For one particular proportionality, and one only, this curve gradually becomes horizontal as it approaches the axis for zero concentration; that is, it neither dips nor rises. If the proportionality be greater than this critical value, the curve would rise more and more rapidly, while if a smaller proportionality be taken, the curve would descend (in a manner similar to the actual experimental curve). It seems feasible, as a working hypothesis, to regard the critical curve so obtained as giving us the k/m curve which would have indicated the conductivity, had the ionisation of the water remained unaltered.

We can now calculate the change in the migration constant which results from the diminution in conductivity—assuming that diminution to be due to the decrease in velocity of one of the ions.

Let u and v be the velocities of the anion and cation respectively, u being variable. Then at any particular concentration, the conductivity k of the acid is equal to $c(u+v)$, where c is a constant. The transport ratio μ for the anion is equal to $v/(u+v)$. Thus μk is equal to cv , and is therefore constant.

Let μ_1 and k_1 refer to the experimental curve, and μ_2 and k_2 to the theoretical one. We regard μ_2 as remaining constant. Its numerical value is obtained from experiments on solutions for which k_1 and k_2 are practically equal, for then $\mu_2 = \mu_1$. For any particular concentration we now have k_1 , k_2 , and μ_2 ; hence μ_1 , the actual migration constant, is obtained.

The process described above of plotting the theoretical curve was carried out with the k/m curve given in the paper already referred to.* Since certain impurities have a considerable effect in lowering the conductivity, it seemed feasible to take the highest curve which consistently resulted from experiment, and regard the lowness of others as being due to impurities.

The following values were then obtained, the value of μ_2 being taken as 0.186.

Concentration (gramme-equiv. per litre).	k_2 (theoretical).	k_1 (experimental).	$u_1 = \frac{k_2}{k_1} u_2$.
0.001	367	365	0.187
0.0005	378	374.5	0.1875
0.0002	387	378.5	0.190
0.0001	389	373.5	0.1935
0.00005	390	358.5	0.2025
0.00003	390.5	339.5	0.214

The "theoretical" migration curve, plotted from the figures in the last column of this table, is shown in the following diagram as a smooth line, and the experimental values obtained (Column VIII of table in § 4) are indicated by crosses.

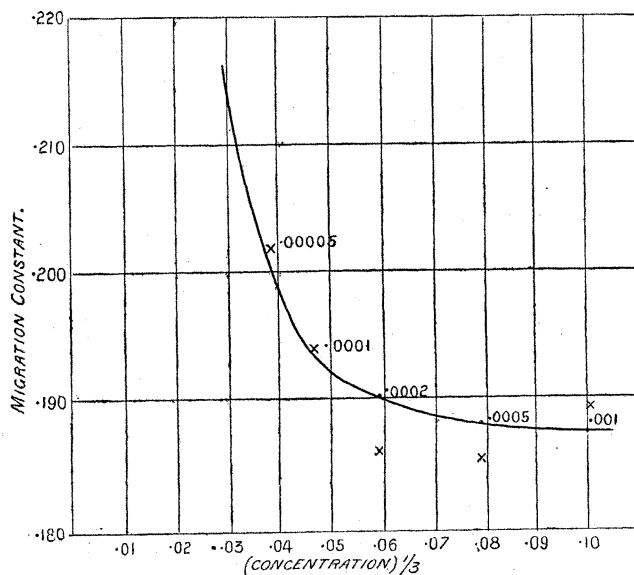


FIG. 4.

* Whetham, 'Roy. Soc. Proc.' A, vol. 76, p, 582, 1905.

1908.] *Properties of Dilute Solutions of Sulphuric Acid.* 73

§ 6. It was thought at first that these experiments gave fresh evidence in favour of the theory that the velocity of the hydrogen ion is diminished at extreme dilution, and that this diminution accounts for the drop in the k/m curve. The extent of the change observed in the migration constant seemed strongly to favour this explanation. Further examination, however, including a calculation of the effect of impurities, shows that the theory receives no support from these experiments, the whole of the rise attributed to the migration constant being readily accounted for when we take into consideration the residual conductivity of the water. Let us, then, consider the problem from the standpoint of a supposed unaltered migration constant.

Let us imagine the conductivity of the distilled water to be due to the presence of some substance AB which becomes ionised in the solution. For all the substances likely to constitute this impurity, hydrogen will be evolved at the cathode, and oxygen at the anode, when the solution is electrolysed. As in the electrolysis of sulphuric acid, the total quantity of solute will remain constant, and the change at the anode will be balanced exactly by that at the cathode. Consider a solution of sulphuric acid containing m gramme-equivalents of the acid per cubic centimetre, and let there be, in this solution, n gramme-equivalents of the substance AB in the ionised state.

Let u be the velocity of the H ion, v of the (SO_4) ion, u' of the A ion, v' of the B ion; we have $u = 319$, $v = 73$, as deduced from the "limiting" equivalent conductivity and the migration constant of sulphuric acid.

The conductivity of the solution is $m(u+v) + n(u'+v) = K$, say. Suppose 1 gramme-equivalent of hydrogen to be liberated at the cathode. Distributing the conductivity amongst the several ions, we deduce the following changes in the anode region:—

mv/K grm.-equiv. of SO_4 ions enters; nv'/K grm.-equiv. of B ions enters;
 mu/K grm.-equiv. of H ions leaves; nu'/K grm.-equiv. of A ions leaves.

Also by the action on the water of the SO_4 and B ions, liberated at the anode, 1 gramme-equivalent of H ions are formed. Hence, in the anode region, there is a net gain of H ions amounting to $\{mv + n(u' + v')\}/K$ gramme-equivalent.

Hence the total conductivity of the solution at the anode is increased by the amount

$$[mv \cdot v + nv' \cdot v' + \{mv + n(u' + v')\}u - nu' \cdot u'] / K,$$

which is $\{mv(u+v) + n(u'+v')(u+v'-u')\} / K$.

If instead of drawing the "equivalent conductivity" curve in the usual way, we plot the specific conductivity (k) against the concentration (m), we shall find that the curve so drawn is a straight line (not passing through the

origin). Hence the increase in conductivity is interpreted as being directly proportional to the increase in the concentration, and consequently (for equal quantities of hydrogen evolved at the cathode) directly proportional to the migration constant, as measured in these experiments.

For pure water and sulphuric acid, $n = 0$, and the increase in the conductivity becomes $mv(u+v)/m(u+v) = v = 73$.

The conductivity of the water used was about 10^{-6} . Let us regard this for the moment as being wholly due to the impurity present. For acid substances, like carbonic acid, which are only slightly ionised and have an ion in common with sulphuric acid, this number must be reduced to indicate the conductivity of AB in the acid solution, as the presence of the sulphuric acid diminishes the ionisation of carbonic acid. For the corresponding saline substances (sulphates) the suppression would be inappreciable.

1. If the impurity be free acid, we have $u = u'$, and the above expression reduces to $\{mv(u+v) + nv'(u+v')\}/K$. For the weakest solutions of sulphuric acid used, the conductivity was 18×10^{-6} , so that

$$m(u+v) = 18 \times 10^{-6}, \quad n(u+v') = 1 \times 10^{-6}$$

Hence the expression for the increase in conductivity becomes

$$(18v+v') \times 10^{-6} / 19 \times 10^{-6},$$

which is never much greater than v , since there are no anions (with the exception of the hydroxyl ion) which have a velocity appreciably greater than that of the sulphate ion. Hence the increase in conductivity at the anode, and the decrease at the cathode, is never appreciably greater than it is when no such impurity is present. With ions for which $v' < v$, the migration constant would appear to be diminished. The extreme effect for the above concentrations of sulphuric acid would be 1 part in 19 (*i.e.*, $v' = 0$), reducing the measured value of the migration constant from 0.186 to 0.176. For any real ions, however, v' is never less than about 40, so that the migration constant would never appear to be less than about 0.182. For very weak acids (*e.g.*, carbonic acid) all such effects are very much reduced, as their "partial conductivity" would be much less than 10^{-6} in the presence of the sulphuric acid. We may conclude, therefore, that the presence of acid impurities in the water used as solvent cannot explain the large increase observed in the migration constant.

2. If the impurity in the water consisted of free alkali, it would be neutralised by the acid, the hydroxyl and hydrogen ions disappearing from solution. We shall find that, though the presence of traces of salt, such as potassium chloride, has no effect on the partial conductivity of the acid, yet it has a very pronounced effect upon the transport ratio as measured in the previously described experiments.

1908.] *Properties of Dilute Solutions of Sulphuric Acid.* 75

As before, we have the formula for the increase in conductivity at the anode,

$$\{mv(u+v) + n(u'+v')(u+v'-u')\}/K.$$

Since u ($= 319$) would always be large compared with $(v'-u')$, we may get an approximate value for this expression, writing it

$$\{mv(u+v) + nu(u'+v')\}/K.$$

Since H and (OH) ions are excepted, v' and u' , even in extreme cases, would never differ by more than 30, and hence the maximum error we introduce by taking this approximation is about 1 in 50, thereby making the transport ratio uncertain to the extent of three or four units in the third decimal place. On the theory to be suggested later, there is practically no difference between v' and u' , so that the approximation is nearly exact. Putting in the values as before, we get $\{18 \times 10^{-6} \times 73 + 319 \times 10^{-6}\} / \{18 \times 10^{-6} + 10^{-6}\} = 86$. Hence for a solution of this strength, the migration constant appears to be increased in the ratio 86/73, *i.e.*, from 0.186 to 0.219.

This rise is greater than that actually observed. Hence, to explain the experimental results, it is only necessary to assume that about half the conductivity of the water used is due to (alkaline or) saline impurity. That such impurity should be present is more than likely; if present, its effect as described above is certain.

The physical explanation of the result of the above analysis is as follows. If the conductivity of the water (10^{-6}) were due to the presence of sulphuric acid, the migration constant would be unaffected. When the ion A replaces the hydrogen ion, a much larger number of molecules (between three and four times as many) is required to make up the initial conductivity, 10^{-6} . Hence, in the migration, between three and four times as many B ions enter the anode region as before. Since the increase in conductivity of the solution at the anode is nearly proportional to the number of SO_4 and B ions entering the region, and since the proportion of B ions to SO_4 ions for these concentrations of sulphuric acid is quite appreciable, and the velocities of the two ions of the same order, it follows that we should expect a marked effect on the change in conductivity from which the migration constant is deduced.

§ 7. The experimental results obtained, therefore, give no evidence in favour of the rise in the true migration constant of sulphuric acid at extreme dilutions; the whole of the apparent rise can be explained logically in a more simple way. In fact, these experiments point rather to a constant value for the transport ratio, though they would not be inconsistent with a gradual decrease in that ratio.

The above analysis also explains why the results for individual experiments

sometimes varied rather widely from the mean: the supposition that a slight variation in the amount of impurity occurred, owing to the absorption of ammonia from the air, for example, being sufficient for the purpose. Also, it was noticed throughout the research, though the fact had to be left unexplained at the time, that experiments performed with different portions of the same-prepared solution generally gave results which agreed better amongst themselves than with those deduced from the use of other specimens of solution of practically the same strength. That still greater irregularity was not shown is accounted for by the fact that the various specimens of distilled water were always prepared in similar conditions, and the conductivity never varied more than 1 part in 20 from the average.

8. *The Conductivity Curve.*

We are thus led to consider once more the cause of the drop in the equivalent conductivity curve. The evidence seems conclusive against the supposition that the presence of carbonic acid, or indeed of any other acid, is sufficient to explain the phenomenon.

In the same series of experiments as those with exhausted water, referred to in the first part of the paper, the effect of the presence of carbonic acid deliberately introduced into the solution was ascertained.* If instead of plotting the k/m curve as was there done, we plot the total conductivity of the solution against the concentration of sulphuric acid—both for the solution containing carbonic acid, and that made up from the pure distilled water—we shall find that the curve for the former case always lies above that for the latter, the two gradually merging as the concentration increases. The difference between the ordinates of the two curves at any particular concentration gives us the effect of the carbonic acid on the conductivity. The effect is always positive, but diminishes in magnitude as the concentration of the sulphuric acid increases. This is explained simply and logically on the supposition that the carbonic acid behaves as a “second acid,” contributing its partial conductivity to the whole conductivity of the solution. Since it is a very weak acid, its ionisation is suppressed by the hydrogen ions of the sulphuric acid, and hence its effect will become less and less, ultimately becoming negligible, as the concentration of the sulphuric acid increases. Hence, by subtracting the full initial conductivity of the solvent containing carbonic acid, we make the partial conductivity of the sulphuric acid appear smaller than it really is, and thus apparently get a drop in the k/m curve. If the purest distilled water contained carbonic acid, the presence of this

* ‘Roy. Soc. Proc.,’ A, vol. 76, p. 580.

1908.] *Properties of Dilute Solutions of Sulphuric Acid.* 77

impurity would explain part of the drop observed, but there remains an excess effect to be accounted for in another way.

For let us consider the equivalent conductivity curve for a solution made up with the purest water obtained by distillation in air. If, instead of deducting the conductivity of the solvent, we take the total conductivity of the solution in plotting the k/m curve, we shall find that the curve still falls off at extreme dilutions. Since the effect of carbonic acid is always additive, correcting for it, to get the true conductivity of the sulphuric acid, can only exaggerate the drop in this curve. Hence, on the basis of any known phenomenon, the presence of carbonic acid, or of any other free acid, is insufficient to explain the whole of the apparent diminution in the conductivity of the sulphuric acid.

Water distilled *in vacuo* has a much smaller conductivity than that distilled in air; hence most of the impurities in the latter are dissolved from the air. Now the atmospheric gases most likely to be dissolved in any appreciable quantity are carbonic acid and ammonia. Normally there is forty times as much carbonic acid as ammonia in the atmosphere, but the solubility of ammonia is so much greater than that of carbonic acid that the quantities of each which would be present in solution are probably of one and the same order.

Let us, then, regard the solvent as containing ammonium carbonate, which at such dilution would be largely in the ionised state. The addition of a strong acid will result in the formation of un-ionised carbonic acid—the ammonium ions remaining in solution. Some of the hydrogen ions of the strong acid have thus been removed. We may regard the first small quantity of acid added as being removed from the solution or rendered inactive, and the partial conductivity as due to the portion left.

Again, instead of adding an acid, let us introduce a strong alkali like potash. Here we shall have un-ionised ammonia (or ammonium hydrate) formed, and some of the hydroxyl ions of the strong alkali will be removed from the solution. As before, the effect is the same as though the first portion of alkali added had been nullified.

This view is best made evident from the conductivity curve—plotting the “partial conductivity” of the acid (the conductivity of the solution minus the initial conductivity of the solvent) against the mass of acid added. A quantitative as well as a qualitative agreement with facts may be observed. The curve is a straight line. When produced it does not pass through the origin, but cuts the axis of zero conductivity at a point showing the concentration of acid to be 4.7×10^{-6} gramme-equivalent per litre (for a curve plotted during the course of the experiments described in this paper). The

effect on the conductivity therefore is the same as though this quantity of acid had been neutralised or removed from solution. Now from the migration constant experiments, since the rise in the measured migration constant was only half what we should expect if the whole of the conductivity of the solvent had been due to saline matter, we may conclude that about half this quantity of salt was present in the water, giving a conductivity of about 5×10^{-7} . Suppose this salt to be ammonium carbonate. The velocity of the CO_3 ion (deduced from the migration constants of potassium and sodium carbonates and sulphates) is about 50, while that of the (NH_4) ion (deduced in a similar manner from the figures for ammonium chloride, etc.) is about 70. Hence $u + v = 120$. We then get $k = m(u + v) = 5 \times 10^{-7}$, so that $m = 5 \times 10^{-7}/120 = 4.2 \times 10^{-9}$ gramme-equivalent per cubic centimetre, or 4.2×10^{-6} gramme-equivalent per litre.

If this be the quantity of ammonium carbonate present in solution, it would account for the neutralisation of an equivalent quantity of sulphuric acid. The agreement with the number deduced from the conductivity curve is very close indeed.

It was also noticed that, when exposed to the air, the conductivities of dilute solutions of acid diminished, often at a considerable rate. That no solution of alkali from the glass produced this effect was shown by preventing the air from getting into contact with the solution, when the conductivity remained quite constant. This seems to show that ammonia, or some other alkali, is readily absorbed from the atmosphere—the hydrogen ions being replaced by ammonium ions in the solution, and the total conductivity being diminished.

There is an objection which must be faced. A solution of ammonium carbonate, on boiling, gives off ammonia and carbonic acid. Hence, in the exhaustion experiments described in the first part of this paper, when the conductivity of the solvent was considerably reduced before the addition of the sulphuric acid, we might have expected that some of the ammonium carbonate would have been abstracted, and the effect made apparent on the k/m curve. It must be remembered, however, that the last traces of ammonia would be removed only with great difficulty. Further, from the above calculations it would appear probable that half the conductivity of the solvent is due to the presence of something which does not affect the transport ratio. If this represents an excess of carbonic acid, the results are explained. Since ammonia is much more soluble than carbonic acid, the latter would be evolved much more readily on exhausting the water. Hence the diminution in conductivity would be accounted for by the removal of the carbonic acid, while the ammonia present may be almost unaffected.

9. We have sought to explain the apparent diminution in the equivalent conductivity of acids (and similarly of alkalies) at extreme dilution by the association of ions brought together in solution. Such an association would take place if the solvent contained: (1) a weak acid such as carbonic acid, (2) a weak alkali such as ammonia, or (3) a salt formed by the neutralisation of a weak acid by a weak alkali, such as ammonium carbonate. We have seen that experimental evidence is opposed to the supposition that the presence of carbonic acid alone is sufficient to explain the phenomenon; we have concluded that the presence of ammonium carbonate is capable of providing this explanation. It has been shown that the diminution in the equivalent conductivity would be accounted for if by some means the conductivity of 4.7×10^{-6} gramme-equivalent of sulphuric acid per litre were destroyed. Hence the "impurity" in the water must be such as will produce this electrical effect. Now consider the three cases. In the first, we should get approximately the same result electrically, if there were 5×10^{-6} gramme-equivalent of ionised carbonic acid per litre of the solvent, which becomes un-ionised on the addition of the strong acid; in the second, 3.5×10^{-6} gramme-equivalent of ionised ammonia per litre would be sufficient; and in the third, 5×10^{-6} gramme-equivalent per litre of ammonium carbonate—also in the ionised state. The conductivities of these solutions would be

$$\begin{aligned} (1) \quad k_1 &= 5 \times 10^{-9} (319 + 50) = 1.8 \times 10^{-6}, \\ (2) \quad k_2 &= 3.5 \times 10^{-9} (184 + 70) = 0.9 \times 10^{-6}, \\ (3) \quad k_3 &= 5 \times 10^{-9} (70 + 50) = 0.6 \times 10^{-6} \end{aligned}$$

The actual conductivity of the water was between 0.9×10^{-6} and 1.0×10^{-6} . Hence there could not have been sufficient carbonic acid present in the free state in the distilled water to account for the observed "diminution" in the conductivity of the solution. The conductivity of the water easily allows for the presence of sufficient ammonium carbonate. The case for ammonia is just on the border line. The high velocities of the hydrogen and hydroxyl ions make the number of gramme-equivalents of an acid or alkali required to produce a given conductivity less than that of a salt. That is why, for a given conductivity, ammonium carbonate is more effective in reducing the conductivity of the solution of sulphuric acid than ammonia or carbonic acid present separately.

We have assumed throughout this final investigation that the velocities of the ions remain constant for the greatest dilutions. It is still possible that these velocities diminish, and that the above explanation only partially accounts for the drop in the k/m curve. To complete the solution of the

problem, it would be necessary, either to obtain an exact knowledge of the impurities in the water, so as to allow for their effect, or to use water which contained no such impurities. In the water distilled in air it is probable that ammonia and carbonic acid are dissolved; if so, the effect in diminishing the conductivity necessarily follows.

Studies of the Processes operative in Solutions.—Parts VI—X.

By Professor H. E. ARMSTRONG, F.R.S. and others.

(Received and Read June 18, 1908.)

[*International Catalogue of Scientific Literature.*

Authors' title slips :—C D VI—X.

- VI D 7050 Title.
- D 7175 Nature of the process of dissolution.
- D 7275 } Explanation of electrolytic conductivity.
- C 6250 }
- D 7090 (Hydrolysis) Title.
- D 7090 (Neutralisation) Interaction of acids and alkalies explained on association hypothesis.
- D 7260 The ionic association hypothesis.
- D 7170 Viscosity, explanation of.
- D 7300 Optical properties and the association hypothesis.
- VII D 7065 Title.
- D 7090 (Hydrolysis) Title.
- D 7275 Title.
- VIII D 7090 (Hydrolysis) Title.
- D 7190 Degree of hydration of salts in solution.
- IX D 7315 Title.
- D 0910 } Polarimeter appliances.
- C 4000 }
- X D 1820 Title.
- D 7275 Title.
- D 7315 Title.

VI.* *Hydrolysis, Hydrolation and Hydronation as Determinants of the Properties of Aqueous Solutions.* By H. E. ARMSTRONG, F.R.S.

In this communication I desire to take a definite step towards an explanation of the fundamental changes attending dissolution and other operations in

* No. I, 'Roy. Soc. Proc.,' A, vol. 78, 1906, pp. 272—295; II—V, 'Roy. Soc. Proc.,' A, vol. 79, 1907, pp. 564—597.